

Some Double Halides of Tin

with the

Aliphatic Amines

and with

Tetramethylammonium

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES
OF THE JOHNS HOPKINS UNIVERSITY

BY

CHARLES GILPIN COOK

1898

EASTON, PA.
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Baltimore

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ACKNOWLEDGMENT.

This investigation was undertaken at the suggestion of Professor Remsen, and I would here express to him my thanks for his kind advice and assistance during the prosecution of the work. I would also thank Professors Morse, Clark, and Ames, for their generous instruction.

SOME DOUBLE HALIDES OF TIN WITH THE ALIPHATIC AMINES AND WITH TET- RAMETHYLAMMONIUM.

Introduction.

The following investigation is one of a series which have been conducted in this laboratory during the past twelve years for the purpose of better understanding the nature of double halides. This subject has claimed the attention of chemists for many years, and as early as 1826 we find, in a letter from Von Bonsdorff¹ to Gay-Lussac, a reference to the difference between acidic and basic halides, and descriptions of certain double halides formed by the union of these. Boullay,² in a paper which appeared the same year, suggests that the two kinds of halides unite, as the two kinds of oxides do, to form salts. Liebig,³ on the other hand, was inclined to oppose this view, and Berzelius⁴ also, not being able to reconcile the accepted definitions with the idea that a compound can at the same time be an acid and a salt, gave his voice against the theory. Condemned thus by two of the greatest chemists of the times, the views of Von Bonsdorff and Boullay did not meet with general acceptance. The idea was again revived by Dr. Hare, of Philadelphia, and discussed in 1840 in his compendium. He says, "Chloro-salts are generally obtained by mingling chloro-acids with chloro-bases, either in the wet or dry way." He also speaks of "bromo-salts" and of "iodo-salts" being formed in a similar manner.

During the fifty years which followed the publication of the above-quoted extract, we find occasional efforts to explain the structure of double halides, but none which met with general favor. Among those who attacked the problem, Naquet⁵ was

¹ Ann. chim. phys., [2], 34, 142.

² *Ibid.*, [2], 34, 337.

³ *Ibid.*, [2], 35, 68.

⁴ Berz. Jsb., 8, 138.

⁵ In his "Principes de Chimie fondée sur les Théories Modernes."

the first to suggest that two halogen atoms, acting together like the linking oxygen atom, unite the basic and acidic portions of the molecule. Blomstrand¹ held a similar view but regarded the halogen as trivalent. Jørgensen² in explaining the constitution of chlorplatinic acid expressed the same idea.

Mallet³ showed that the specific gravity of hydrofluoric acid gas at 30° indicates its formula to be H_2F_2 , and from this he derives the same explanation of the double fluorides. Kolbe,⁴ Francke⁵, Cooke⁶, Armstrong,⁷ and Hayes⁸ have held similar views.

In 1889, Professor Remsen⁹ gave new impetus to double halide research by the publication of an article on the "Nature and Structure of the Double Halides." In this article he showed clearly on what a wide basis of fact the views first advanced by Naquet are founded, and pointed out that, with a few exceptions, all double halides then known were included under the following law. "When a halide of any element combines with a halide of any alkali metal to form a double salt, the number of molecules of alkali salt which is added to one molecule of the other halide is never greater and is generally less than the number of halogen atoms combined in the latter." Subsequent work has confirmed this law. Supposed exceptions have been investigated and in many cases found to have no existence. Numerous new double halides have been made, nearly all of which conform to the above law. The exceptions can, in general, be covered by the assumption that, in them, three halogen¹⁰ atoms play

the part of a trivalent group, $-\text{Cl} \begin{array}{c} \diagup \text{Cl} - \\ | \\ \diagdown \text{Cl} - \end{array}$, the compound

$\text{CuCl} \cdot 2\text{KCl}$ being expressed thus: $\text{Cu}-\text{Cl} \begin{array}{c} \diagup \text{ClK} \\ | \\ \diagdown \text{ClK} \end{array}$.

¹ In his "Chemie de Jetztzeit."

² J. prakt. Chem., **16**, 352.

³ Am. Chem. J., **3**, 189 (1881).

⁴ In his "Kurzes Lehrbuch der anorganischen Chemie."

⁵ Francke: J. prakt. chem. [N. F.], **36**, 451.

⁶ In his "Principles of Chemical Philosophy."

⁷ British Assoc. Reports (1885), 959.

⁸ Phil. Mag. [5], **25**, 221, 297.

⁹ Am. Chem. J., **11**, 291.

¹⁰ *Ibid.*, **14**, 87.

The work has been extended to the halides of the heavy metals with halogen salts of the substituted ammonias and the present investigation is a continuation of it in that direction.

Preparation of Material.

Amines.—The bases were obtained from the salts prepared by Bender and Hobein.

Tetramethylammonium hydroxide was prepared from its salts by treatment with moist silver oxide according to Hofmann's method¹ and the required salt obtained by neutralizing with the corresponding acid.

Stannous chloride and bromide were made by dissolving the metal in hydrochloric and hydrobromic acids.

The stannic chloride used had been previously prepared by passing chlorine over tin, and was purified by distillation from tin.

Stannic bromide was obtained by the action of bromine on tin. The bromine was allowed to fall, drop by drop, on granulated tin contained in a retort. The reaction, which required but a gentle heat for its initiation, was very violent and continued so long as bromine was added. The product mixed with excess of bromine, distilled over into the receiver and after being purified by fractional distillation was a liquid of light yellow color which, on cooling, solidified in beautiful white crystals.

Methods of Analysis.

Tin in chlorstannites was determined by dissolving in hydrochloric acid solution of ferric chloride, heating to boiling, diluting with water, cooling, and titrating the ferrous chloride (formed by the reduction of the ferric chloride) with standard potassium permanganate solution.

Stannic tin was determined by reducing to metallic state with zinc and hydrochloric acid and treating the reduced metal as above. In a few cases tin was estimated as the oxide by evaporating the salt in a weighed crucible with nitric acid and incinerating the base according to the method of

¹ J. Chem. Soc., 4, 307.

Carnelly and O'Shea¹ for determination of tin in stannic bromide, but the method was not found satisfactory.

Amines were estimated by decomposing the salts with sodium or potassium hydroxide and distilling with the aid of steam. The distillate was collected in a known quantity of standard acid and the excess of acid titrated with standard potassium hydroxide solution. For the distillation, a gang-still composed of four block-tin coils cooled in a water-tank was used. The method was found both exact and rapid.

The tin of bromstannites was determined by reduction as in the case of stannic salts, since the hydrobromic acid prevented the use of the method applied to chlorstannites.

Preparation of Double Salts.

Concentrated solutions of the two salts were mixed in small beakers in various molecular proportions, as 1 : 1, 1 : 2, 3 : 2, 4 : 1, etc. The mixtures, after being acidulated with the corresponding acids, were evaporated, either by heating or in sulphuric acid and caustic soda desiccators. The successive homogeneous crops of crystals were dried by pressing between folds of drying-paper and analyzed.

Compounds Described.

- 1 : 1 Methylamine chlorstannite.
- 2 : 1 Methylamine chlorstannate.
- 1 : 1 Dimethylamine chlorstannite.
- 2 : 1 Dimethylamine chlorstannate.
- 1 : 1 Trimethylamine chlorstannite.
- 2 : 1 Trimethylamine chlorstannate.
- 1 : 1 Tetramethylammonium chlorstannite.
- 2 : 1 Tetramethylammonium chlorstannate.
- 1 : 1 Ethylamine chlorstannite.
- 2 : 1 Ethylamine chlorstannate.
- 1 : 1 Triethylamine chlorstannate.
- 2 : 1 Triethylamine chlorstannate.
- 3 : 1 Triethylamine chlorstannate.
- 1 : 1 Methylamine bromstannite.
- 2 : 1 Methylamine bromstannate.

¹ J. Chem. Soc., **33**, 55.

- 1 : 1 Dimethylamine bromstannite.
 2 : 1 Dimethylamine bromstannate.
 2 : 1 Trimethylamine bromstannate.
 1 : 1 Ethylamine bromstannite.
 2 : 1 Ethylamine bromstannate.
 2 : 1 Triethylamine bromstannate.

DOUBLE CHLORIDES.

Methylamine Salts.

1 : 1 *Methylamine chlorstannite*, $\text{CH}_3\text{NH}_2\text{SnCl}_3$.—This salt was obtained from a number of mixtures of methylamine hydrochloride and stannous chloride. The crystals were well defined, transparent, and prismatic in form. Their crystallographic measurements, however, were not made. The salt is much less soluble than stannous chloride, as is shown by the fact that in a few cases the excess of stannous chloride crystallized out in nearly pure condition. Analysis :

	Calculated for $\text{CH}_3\text{NH}_2\text{SnCl}_3$.	I.	Found. II.	III.
NH_3CH_3 ,	12.52	12.51		12.48
Sn	46.01	45.98	45.99	

2 : 1 *Methylamine chlorstannate*, $[\text{CH}_3\text{NH}_2]_2\text{SnCl}_6$.—Several beakers containing mixtures of methylamine hydrochloride and stannous chloride became oxidized by the air, and crystals were formed which showed, on analysis, to be 2 : 1 methylamine chlorstannate. This salt had been described by Hiortdahl.¹ In one of these beakers a small crop of white pellets mixed with other crystals was formed. These were separated mechanically, and a determination of the base seeming to indicate a 1 : 1 stannic salt, an extensive investigation was undertaken to obtain this salt in sufficiently large quantity for complete analysis. For this purpose a series of mixtures of methylamine hydrochloride and stannic chloride were made and the successive crops of crystals analyzed, but all analyses indicated the 2 : 1 salt only. The crystals seemed to be of two forms : the one form, hexagonal rhombohedral, as described by Hiortdahl, the other, transparent scales.

¹ Zeit. für Kryst., 6, 462.

	Calculated for $[\text{CH}_3\text{NH}_2]_2\text{SnCl}_6$	I.	Found. II.	III.
CH_3NH_2	16.23	16.20	16.25	
Sn	29.86	30.03		30.16

Dimethylamine Salts.

1 : 1 *Dimethylamine chlorstannite*, $(\text{CH}_3)_2\text{NH}_2\text{SnCl}_3$.—When concentrated solutions of dimethylamine hydrochloride and stannous chloride are mixed, this salt forms in needle-like crystals. In some cases the crystals seemed to be rhombic, but none could be obtained suitable for crystallographic work. In two beakers the excess of stannous chloride crystallized out in nearly pure form showing the difference of solubility of the two salts.

	Calculated for $(\text{CH}_3)_2\text{NH}_2\text{SnCl}_3$	I.	Found. II.	III.
$(\text{CH}_3)_2\text{NH}_2$	17.04	17.11		17.06
Sn	43.61		43.64	43.65

2 : 1 *Dimethylamine chlorstannate*, $[(\text{CH}_3)_2\text{NH}_2]_2\text{SnCl}_6$.—A number of mixtures of dimethylamine hydrochloride and stannous chloride, made for the purpose of obtaining chlorstannites, became oxidized. In these, crops of transparent crystals formed. These on analysis proved to be the 2 : 1 dimethylamine salt described by Hiortdahl¹.

Further work showed that this salt crystallizes from all mixtures of dimethylamine hydrochloride and stannic chloride on concentration. The salt formed in four-sided tables generally. Analysis :

	Calculated for $[(\text{CH}_3)_2\text{NH}_2]_2\text{SnCl}_6$	I.	Found. II.	III.	IV.
$(\text{CH}_3)_2\text{NH}_2$	21.79	21.7	21.8		
Sn	27.88			27.81	27.71

Trimethylamine Salts.

1 : 1 *Trimethylamine chlorstannite*, $(\text{CH}_3)_3\text{NHSnCl}_3$.—This salt is difficultly soluble and comes down almost quantitatively as a white precipitate from mixtures of concentrated solutions of its constituents. From more dilute solutions, however, crystals in the form of triangular plates were formed. No

¹ Zeit. für Kryst., 6, 464.

specimens were obtained suitable for crystallographic work. A large number of determinations of base and tin were made, many of which indicated the 1 : 1 salt.

	Calculated for (CH ₃) ₃ NHSnCl ₃ .	I.	Found. II.	III.	IV.
(CH ₃) ₃ NH	21.13	21.07		21.09	
Sn	41.46		41.57		41.58

2 : 1 *Trimethylamine chlorstannate*, [(CH₃)₃NH]₂SnCl₆.—This salt was obtained from a number of mixtures of trimethylamine hydrochloride and stannous chloride which became oxidized by the air. The salt had been previously made by Hiortdahl.¹ The crystals were well formed and often of quite good size. Their form is a combination of the cube and octahedron.

	Calculated for [(CH ₃) ₃ NH] ₂ SnCl ₆ .	I.	Found. II.	III.
(CH ₃) ₃ NH	26.66	26.51		26.81
Sn	26.15		25.72	

Tetramethylammonium Salts.

1 : 1 *Tetramethylammonium chlorstannite*, (CH₃)₄N₂SnCl₃.—This salt is formed in all mixtures of the chloride of the base with stannous chloride. The salt is precipitated from moderately concentrated solutions in the form of a crystalline powder, which is dried with difficulty by pressing between folds of drying-paper. In more dilute solutions the crystals took the form of needles. Those solutions which contained an excess of the chloride of the base were easily oxidized during evaporation.

	Calculated for N(CH ₃) ₄ SnCl ₃ .	I.	Found. II.
Sn	39.51	39.59	39.37

2 : 1 *Tetramethylammonium chlorstannate*, [N(CH₃)₄]₂SnCl₆.—When moderately concentrated solutions of stannic chloride and tetramethylammonium chloride are mixed in any proportion a salt is formed which is shown by analysis to have the above formula. The crystals are generally small and are not easily soluble in hot, dilute hydrochloric acid. From this solution the salt recrystallizes, on cooling, in beautiful, brilliant

¹ Zeit. für Kryst., 6, 466.

crystals which are a combination of the cube and octahedron.
Analysis :

	Calculated for [N(CH ₃) ₄] ₂ SnCl ₆ .	I.	Found. II.	III.
Sn	24.62	24.3	24.35	
Cl	44.43			44.21

Specimens suitable for crystallographic measurements were obtained and the results will be given in a future publication.

Ethylamine Salts.

1 : 1 *Ethylamine chlorstannite*, NH₃C₂H₅SnCl₅.—This salt was easily formed when concentrated solutions of the hydrochloride of the base and stannous chloride were mixed in various proportions. If the solutions were not too concentrated, the salt formed in white needles soluble in dilute acid. Quite dilute solutions generally became oxidized during evaporation and gave crops of crystals mixed with a stannic salt or composed entirely of the stannic salt. No specimens could be obtained suitable for crystallographic work. Analysis showed the salt to be isomeric with the 1 : 1 dimethylamine chlorstannite.

	Calculated for C ₂ H ₅ NH ₃ SnCl ₅ .	I.	Found. II.	III.
C ₂ H ₅ NH ₃	17.04	17.09	16.99	
Sn	43.61	43.52		43.61

2 : 1 *Ethylamine chlorstannate*, [C₂H₅NH₃]₂SnCl₆.—The crystals obtained from the oxidized solutions of ethylamine hydrochloride and stannous chloride, mentioned above, as well as from a number of mixtures of stannic chloride and the hydrochloride of the base in various proportions, were found, on analysis, to be the same salt—the 2 : 1 ethylamine chlorstannate. This is isomeric with the 2 : 1 dimethylamine chlorstannate and, like it, crystallizes well. The crystals are made up of combinations of pyramidal and prismatic faces, in some cases the prismatic form occurring to the exclusion of the pyramids while in others the latter predominate giving the crystals an entirely different appearance. The crystals are tough, translucent, and with but little luster.

	Calculated for [C ₂ H ₅ NH ₂] ₃ SnCl ₄ .	I.	Found. II.	III.
C ₂ H ₅ NH ₂	21.79		21.82	21.75
Sn	27.88	27.58 27.52		

Triethylamine Salts.

When triethylamine hydrochloride and stannous chloride were mixed in concentrated solution there was no evidence of the formation of a double salt, and all attempts to concentrate the solution sufficiently for crystallization to take place only led to the oxidation of the tin salt, and the formation of chlorstannates. To prevent this oxidation, an attempt was made to keep the beakers containing the solutions in an atmosphere of carbon dioxide for some weeks, but evaporation was so slow that sufficient oxygen from the air found its way into the solutions to produce oxidation, and chlorstannates were again formed. The crystals formed by the oxidation of all the above-mentioned mixtures, as well as those from mixtures of triethylamine hydrochloride and stannic chloride were, in general, in the form of rhombic plates, joined by their corners into masses. In some cases the individual crystals showed a tendency to curl up, giving the cluster something of the appearance of a rose. A few large well-formed crystals were obtained, which much resembled Iceland spar.

About twenty-four determinations of base were made in the various specimens of crystals, with the most discordant results, and crystals of apparently the same form showed, on analysis, to be mixtures of salts with from one to three molecules of base. In a few samples which proved to be nearly pure 2 : 1 triethylamine chlorstannate the tin and base were determined with reasonably good results as follows :

	Calculated for [(C ₂ H ₅) ₃ NH] ₂ SnCl ₄ .	I.	Found. II.	III.
(C ₂ H ₅) ₃ NH	38.20	38.20	38.35	37.78
Sn	22.03	21.96		22.07

In a number of cases the figures for base were in the neighborhood of those required by the 1 : 1 salt :

	Calculated for (C ₂ H ₅) ₃ NHSnCl ₄ .	I.	Found. II.	III.
(C ₂ H ₅) ₃ NH	25.71	26.94	26.17	26.19

Quite a number of the base determinations ran above the per cent. required for the 2 : 1 salt, and a few approached the value of the 3 : 1 salt :

	Calculated for [(C ₂ H ₅) ₃ NH] ₃ SnCl ₇ .	I.	Found. II.
Base	45.57	44.75	43.85

In almost all cases the crystals had the appearance of those of a pure salt, and in nearly all cases analysis showed them to be mixtures.

DOUBLE BROMIDES.

The preparation of the bromstannites was found to be accompanied with much more difficulty than that of the corresponding chlorine salts. Not only did the solutions oxidize so easily on standing that successive crops of crystals could not be obtained, but also the crystals when removed from the mother-liquor were dried with more difficulty, and in a few cases became oxidized after they had been dried by being pressed between numerous folds of drying-paper. For these, and other reasons, a few of the possible salts were abandoned. The crystals were generally small and of forms difficult to determine.

The bromstannates, on the other hand, are generally beautifully crystallized, and a number of specimens suitable for crystallographic work were obtained.

Methylamine Salts.

1 : 1 *Methylamine bromstannite*, CH₃NH₂SnBr₃.—When quite concentrated solutions of methylamine hydrobromide and stannous bromide are mixed the solution remains clear for a moment and then a bright red precipitate is formed in large quantity. This precipitate dissolves to a colorless, or nearly colorless, solution on the addition of water. From more dilute solutions the salt makes its appearance in the form of dark red, shining scales.

A dilute solution was concentrated by heating, and on cooling, red needles appeared, arranged in the form of cubes with beautifully fringed edges. These crystals, after standing some days in the mother-liquor, were subjected to the method

for determining bases and found to contain a considerable quantity of a bromstannate. Other crystals, which were allowed to stand under similar circumstances, disappeared and a yellow bromstannate took their place. Crystals which were carefully dried soon after precipitation were analyzed and the following results obtained :

	Calculated for $\text{CH}_3\text{NH}_2\text{SnBr}_3$.	I.	Found. II.	III.	IV.
CH_3NH_2 ,	8.22	8.28		8.27	
Sn	30.25		30.36		29.95

2 : 1 *Methylamine bromstannate*, $[\text{CH}_3\text{NH}_2]_2\text{SnBr}_6$.—The crystals of this salt were generally small and not well defined. They formed slowly when mixtures of their constituents were allowed to evaporate spontaneously. Their shape and appearance were quite variable, but analysis showed them to be generally nearly pure. The most common form was that of yellow pellets composed of gummy crystal masses. In a number of cases yellow hexagonal plates were noticed. At other times the salt formed as scales, a few of which were so thin as to appear iridescent.

Among the analyses were the following :

	Calculated for $[\text{CH}_3\text{NH}_2]_2\text{SnBr}_6$.	I.	Found. II.	III.	IV.
CH_3NH_2 ,	9.69	9.63		9.70	
Sn	17.82		18.00		18.20

Dimethylamine Salts.

1 : 1 *Dimethylamine bromstannite*, $(\text{CH}_3)_2\text{NH}_2\text{SnBr}_3$.—This salt was made, from a number of mixtures of dimethylamine hydrobromide and stannous bromide, as a crystalline precipitate in the form of beautiful, brilliant, white scales or feathers. Several times it came down with a light-yellow or brown tint, probably due to impurity in the form of a bromstannate. A number of the base determinations showed a tendency to run high.

	Calculated for $(\text{CH}_3)_2\text{NH}_2\text{SnBr}_3$.	I.	Found. II.	III.
$(\text{CH}_3)_2\text{NH}_2$,	11.41	11.21	11.21	
Sn	29.20			28.93

2 : 1 *Dimethylamine bromstannate*, $[(\text{CH}_3)_2\text{NH}]_2\text{SnBr}_6$.—This salt was made in the usual way by mixing its constituents in a number of proportions and allowing the mixtures to evaporate spontaneously. The crystals, which formed readily and in good size, were brilliant, transparent, hexagonal prisms with modified ends. A number of specimens suitable for crystallographic work were obtained. Their measurements will be published later. Analysis :

	Calculated for $[(\text{CH}_3)_2\text{NH}]_2\text{SnBr}_6$.	I.	Found. II.	III.
$(\text{CH}_3)_2\text{NH}_2$	13.11	13.14		13.14
Sn	17.14	16.76	16.94	

Trimethylamine Salts.

The hydrobromide of the base was mixed with stannous bromide in a number of proportions, and one crop of white, featherlike crystals and needles was obtained from one beaker, but the solutions showed such a tendency to become oxidized that further efforts to obtain the salt were abandoned.

2 : 1 *Trimethylamine bromstannate*, $[(\text{CH}_3)_3\text{NH}]_2\text{SnBr}_6$.—The crystals of this salt were generally small, but under the glass seemed to resemble those of trimethylamine chlorstannate and were probably a combination of cube and octahedron. They were nearly transparent and of a yellow color. Analysis :

	Calculated for $[(\text{CH}_3)_3\text{NH}]_2\text{SnBr}_6$.	I.	Found. II.	III.
$(\text{CH}_3)_3\text{NH}$	16.75	16.39		
Sn	16.43		16.59	16.67

Ethylamine Salts.

1 : 1 *Ethylamine bromstannite*, $\text{C}_2\text{H}_5\text{NH}_2\text{SnBr}_3$.—Owing to the ease with which the solutions of this salt became oxidized, a large number of crops of the crystals were not obtained, but analysis clearly established their composition to be isomeric with the 1 : 1 dimethylamine bromstannite mentioned above. The crystals were of a yellowish white, shining, semitransparent, and needle-like in form.

	Calculated for $C_2H_5NH_2SnBr_6$.	Found.	
		I.	II.
$C_2H_5NH_2$	11.41		11.48
Sn	29.2	29.05	29.46

2 : 1 *Ethylamine bromstannate*, $[C_2H_5NH_2]_2SnBr_6$.—The forms of the crystals of this salt are much like those of the corresponding chlorine salt, but in other characteristics the crystals show more resemblance to the isomeric 2 : 1 dimethylamine bromstannate. They are lustrous, of a bright yellow color, and nearly transparent. In most cases the prismatic faces, and also the pyramidal ones are developed but some crystals on which the pyramidal form predominated were noticed. Specimens for measurement were obtained, and their crystallography will be given in a future publication.

	Calculated for $[C_2H_5NH_2]_2SnBr_6$.	I.	Found.	III.
			II.	
$C_2H_5NH_2$	13.11	13.26		13.37
Sn	17.14		17.15	

Triethylamine Salts.

When triethylamine hydrobromide was mixed with stannous bromide, beautiful, white, lustrous fibers were formed. The crystals were removed from several beakers and dried with difficulty by pressing between folds of drying-paper. After these crystals were dry, or nearly so, they became a bright-yellow which was supposed to be due to oxidation, and further work with this salt was abandoned.

2 : 1 *Triethylamine bromstannate*, $[(C_2H_5)_3NH]_2SnBr_6$.—This salt was obtained in the usual manner, but no specimens of crystals suitable for measurement were obtained. In general the form was that of rhombic plates, somewhat resembling those of the corresponding chlorine salt; they were yellow in color, and in some cases transparent. The percentage of base was in a number of analyses a little high, but there was no evidence of the formation of other salts as in the case of the triethylamine chlorine salts. Analysis :

	Calculated for $[(C_2H_5)_3NH]_2SnBr_6$.	I.	Found.	II.
$(C_2H_5)_3NH$	25.49		25.53	25.53
Sn	14.70	14.77		

CONCLUSIONS.

A marked regularity is found throughout this whole series of salts. All of them, with one exception, belong to the 1 : 1 or 2 : 1 form, and all obey Remsen's Law as first stated. The chlorine and bromine salts show many crystallographic resemblances, though their colors are often different.

The salts containing tin in the stannous condition seem to show differences in the ease with which they are oxidized, but so many modifying influences come in, that no generalizations can be made.

BIOGRAPHICAL.

The author of this dissertation was born near Glenville, Md., November 25, 1866. His early education was received at public and private schools in Harford Co., Md., and at Westtown Boarding School, Pa., where he graduated in 1890. The same year he entered the junior class of Haverford College and in 1892 received the degree of B.S. and the following year that of A.M. During the two years from 1881 to '93 he held the position of Chemical Laboratory Assistant at Haverford College. The year 1893-94 was spent in teaching at Bridgewater College, Va., and 1894-95 as principal of Aurora Academy, N. C. Since October, 1895, he has pursued advanced work in Chemistry at the Johns Hopkins University, having taken Geology and Physics as subordinate studies.

